

**A METHOD TO RECOVER ALGAL BIOMASS USING
MEMBRANE TECHNOLOGIES**

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by

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A METHOD TO RECOVER ALGAL BIOMASS USING MEMBRANE TECHNOLOGIES

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LIST OF SYMBOLS

A	Projected area of the body on the xy plane
A_H	Hamaker constant for the integrated media
D	Diameter
$E(r)$	Interaction energy per unit are between 2 infinite plates
ϵ_r	Relative permittivity of the solution
ϵ_o	Relative permittivity of a vacuum
k_1	Unit vector directed towards the positive z axes of the sphere
k_1	Unit vector directed towards the positive z axes of the cylinder
k	Boltzmann constant
κ	Debye-Hückel parameter of the electrolyte solution
n_1	Outward unit vector normal to the surface of the sphere
n_2	Outward unit vector normal to the surface of the cylinder
r	Separation distance between infinite plates
R_c	Radius of the hollow finer membrane
R_s	Radius of the microalgae
T	Absolute tmepature
θ	angle between the y axis and the line from the surface eleent to the center of the circle
V	Interaction energy
V_{EDL}	electric double layer interaction energy between a membrane and a microalgae
V_{vdW}	van der Waals interaction energy between a membrane and a microalgae
ψ_{o1}	unperturbed surface potential of the microalgae
ψ_{o2}	unperturbed surface potential of the membrane

LIST OF ABBREVIATIONS

CA	Cellulose acetate
CAB	Cellulose acetate butyrate
CAP	Cellulose acetate propionate
CO ₂	Carbon dioxide
DLVO	Derjaguin-Landau-Verwey-Overbeek
EDL	Electric double layer
NO _x	Nitrogen oxides
P84	Polyamide type 84
PAN	Polyacrylonitrile
PE	Polyethylene
PES	Polyethersulfone
PP	Polypropylene
PS	Polysulfone
PTFE	Polytetrafluoroethylene
PVB	Poly(vinylbutyral)
PVDF	Polyvinylidene fluoride
SEI	Surface element integration
vdW	van der Waals

SUMMARY

Environmental awareness has increased significantly during the past years and the need to replace fossil fuels with a more sustainable alternative has become a priority in the modern society. Algal biofuels have shown to have a good productivity compared to other biomass feedstock options but the high cost- low-efficiency cultivation process has proven to be a challenge. The purpose of this project is to use membrane technologies to recover algal biomass more efficiently. This technology would significantly reduce the water usage and energy input to the algal biomass production process.

In this study, the Derjaguin-Landau-Verwey-Overbeek (DLVO) model derived using the Surface Element Integration (SEI) technique was used to identify the interaction energy between 3 microalgae species and 5 hollow fiber membrane materials. The results suggested that *Scenedesmus Obliquus* would have the lowest energy barrier (-2.7834 kT) with a Poly(vinylbutyral) (PVB) hollow fiber membrane, therefore it would have a greater initial number of algal cells attaching to the membrane, compared to the other microalgae and membrane materials studied. Further work needs to be completed in order to integrate algae growth and biomass harvesting into the actual model.

CHAPTER 1

INTRODUCTION

As the energy demand continues to increase around the world, the search for a more sustainable alternative to supply it becomes a priority. According to the BP statistical review of world energy, in 2008, 88% of the primary energy came from fossil fuels while only 5 % and 6% came from nuclear energy and hydroelectricity, respectively [1]. The dependence on fossil fuels has led to the deterioration of the environment and the depletion of natural resources [2].

Fossil fuels are the primary contributors of greenhouse gases into the atmosphere. Greenhouse gases contribute to global warming, one of the main causes of climate change [3]. In addition, greenhouse gases contribute to oceanic acidification because oceans absorb about one third of the CO₂ emitted by anthropogenic activities. As the amount of CO₂ increases in the atmosphere, the pH of the ocean decreases. Acidic water can greatly impact the biodiversity of the ocean and consequently affect human life [4]. These are just two of the negative impacts that come from CO₂ emissions to the atmosphere but as the new economies grow and develop, the energy consumption will increase the environmental damages [5].

Many different alternatives are being studied worldwide in order to challenge these problems. Some examples include: biofuels, geothermal, wind turbines, hydroelectric, and solar energy [6]. Although most of these technologies seem promising, there are still several issues that need to be addressed. The first and probably most important one is the challenge to make these alternatives commercially and economically feasible.

Transportation and energy generation are the main responsible sectors for greenhouse gas emissions into the atmosphere [7]. The task to replace fossil fuels with a

renewable energy source is actively being studied and implemented in order to minimize the negative impact on the environment and improve quality of life. The production of biofuels has proven to be one of the most promising alternatives to the fossil fuel demand for transportation and energy generation. Methods to recover biomass from microalgae are currently being researched for the production of biofuels. Some of these have yielded positive results regarding the volume of the biomass extracted, but no process has shown to be commercially feasible yet.

The objective of this project is to use membrane technologies in order to recover algal biomass by delivering nutrients and CO₂ more efficiently to the microalgae. The first step was to identify the best combination of microalgae and hollow fiber membrane material to be used. This study shows how that selection was made based on a model that calculates the total interaction energy between the membranes and microalgae to identify which microalgae would attach better on the membrane.

This paper first presents an overview of biofuels, microalgae, membrane technologies and current technologies to harvest microalgae. Then, the theoretical aspects of the model used and the results and discussion of the outcomes obtained with the model. Finally, the conclusion based on modeling results and future work to be done for the completion of the rest of the project

CHAPTER 2

LITERATURE REVIEW

Biofuels

Biofuels are a source of energy obtained from renewable biological materials. Some of these include ethanol, corn and algae. Commercially produced biofuels that are currently available, first generation biofuels, come from sugar, starch and/or oilseeds crops. These are fermented to produce bioalcohols such as ethanol and butanol. Biofuels that come from animal fats, also currently available, are processed for biodiesel production. The biofuels that are not produced commercially are second and third generation. Second generation biofuels come from cellulose extracted from non-food crops such as straw and wood. Third generation biofuels come from algae [8].

The production of biofuels is expected to bring many benefits to modern society. These include: employment promotion in rural areas, diverse sources for fuel supply, replacing fossil fuels in the long term and reduced greenhouse gases emissions. Bioethanol and biodiesel are capable of replacing gasoline and diesel, respectively. The replacement can be done using today's technologies for production and distribution systems and requires little variation on car engines [7]. These are some of the reasons why biofuels are one of the most viable alternatives to replace fossil fuels in the short term.

The rapid global growth and production of biofuels is projected to continue in the future years because of policies established by governments and environmental agencies to protect the environment and mitigate greenhouse gases emissions [5]. However, the objective of replacing fossil fuels to meet the current and future energy demand is far from being achieved due to: the competition for the use of land between food and raw

materials for biofuels production, lack of market structures and agricultural management, and high requirements of water and fertilizers [9].

The use of first generation biofuels has created controversy because of the competition with food markets and the possible impact on food security around the world. There are some questions regarding the sustainability of biofuels compared to fossil fuels specially when it comes to the most vulnerable regions of the world [10]. Some of the negative implications that first generation biofuels have are: higher food prices and additional pressure on natural resources that can lead to environmental damage and consequently impact society [11]. About 1% of the current agricultural land around the world is being used for the production of biofuels, which supplies only 1% of fuel demand for transportation. The possibility of increasing the fuel supply to meet transportation demand would have an enormous impact on food crops due to the large arable land required [12].

The use of second generation biofuels would be a better alternative to supply the fuel demand for transportation regarding the aspects mentioned before because food crops are not required. But the process to produce biofuels from wood or straw is not commercially feasible yet due in part to the economic demand of the process. The conditions for a viable biofuel alternative include: it should compete with fossil fuels; require less or no extra land; improve air quality (reduce greenhouse gases emissions); and require minimal water, fertilizer and nutrients use [11]. Microalgae could potentially meet all of these conditions providing, at the same time, environmental benefits [13].

Microalgae

Microalgae are photosynthetic organisms that use solar energy in order to combine water and CO₂ to produce biomass [14]. Algae are known as primitive plants because they lack roots, stems and leaves and their primary photosynthetic pigment is chlorophyll a [15]. They are documented as an old life form, whose structure is mainly

for energy conversion, which allows them to easily adapt to different environmental conditions [16]. Approximately more than 50,000 species of microalgae exist in aquatic and terrestrial ecosystems, but about 60% of these have been studied [17].

Algae can be either prokaryotic or eukaryotic, and can grow under extreme conditions because of their simple structure [7]. Prokaryotic algae do not have membrane-surrounded organelles such as nuclei, mitochondria and flagella, therefore this type of algae share more in common with bacteria than with plants. Eukaryotic algae, on the other side, have the membrane-surrounded organelles that allow them to survive and reproduce [11]. These types of algae are classified according to their pigmentation, cellular structure and life cycle [18]. Some of these classes are: green algae, red algae and diatoms [11]. Algae are either autotrophic or heterotrophic. Autotrophic organisms use inorganic compounds and light energy for growth while heterotrophic ones require a carbon source and nutrients [15].

Researchers in different countries collect microalgae. One of the largest collections is found in Portugal where microalgae is use for several purposes such as: pharmaceutical applications, food crops and energy production [7]. Most collections include different strains and species of both fresh water and saline water microalgae, which allows for multiple studies related to algae. Biofuels production from microalgae is one of the fastest growing research trends because of the challenge to replace fossil fuels with a more sustainable alternative.

Microalgae as an alternative for biodiesel production

Research has shown several advantages of using microalgae for biodiesel production compare to the production of biofuels from other renewable sources. Microalgae are easy to cultivate because they do not require much attention, can use non-potable water and can easily obtain nutrients [7]. Growth cycles for microalgae are very short due to the fast reproduction that occurs from the conversion of solar energy into

chemical energy using photosynthesis [14]. Furthermore, the addition of nutrients and aeration could accelerate the growth rate. Since microalgae easily adapt to a different environment, specific growth characteristics for certain specie can be determined. This is not possible for first generation biofuels [7].

One of the main advantages of biofuel production from microalgae is that the competition for arable land with food crops is reduced because of the high growth rate and productivity of microalgae. For example, the land area required for microalgae growth can be up to 132 times less when compared to the land required to produce biofuels from soybeans [19].

Microalgae cannot only be used for the production of biodiesel, but also for the production of methane, hydrogen, ethanol and other fuels. They can also remove CO₂ from industrial gases while producing biodiesel. Furthermore they can use water contaminants removed from wastewater as nutrient and be processed into different fuels because of the high nitrogen to phosphorous ratio [13].

Another advantage of microalgae is that they can grow in areas that do not work for agriculture because of their ability to survive with little nutrients, through weather changes and in harsh environments [7]. Some microalgae species can produce other compounds that are used in other industries like pharmaceutical and chemical [20]. Microalgae derivatives have different commercial applications that could potentially improve not only biofuel production, but also other biotechnological industries [21].

Biomass production from microalgae

Microalgae can grow under natural or artificial conditions. Natural environments provide sunlight, which supplies carbon dioxide and nutrients to the algae. These can be an advantage because it is a free natural resource but it can also be a drawback because of the seasonal variations and the sunlight cycles [11, 22]. Artificial lights are used for open algae systems in order to address this issue. Nevertheless this solution increases the

energy demand for cultivation and often comes from the use of fossil fuels, which leads to a negative environmental impact [23].

Besides solar energy, microalgae need CO₂ and nutrients like nitrogen, silicon, phosphorous to grow. Microalgae is capable of fixing CO₂ from different sources and nitrogen from NO_x [13, 24, 25]. The other nutrients should be provided because they are not easily available in nature.

Some of the microalgae production mechanisms that are currently being researched and developed include: photoautotrophic, heterotrophic and mixotrophic. The first one is based on autotrophic photosynthesis; the next one requires assimilation of organic compounds and the last one combines both of the previous mechanisms. Biomass production from microalgae can be done with open pond, closed bioreactor or hybrid systems [11].

Biomass recovery from microalgae

In general, biomass recovery from microalgae requires at least one solid-liquid separation step. This is usually the toughest and most expensive phase of the biofuel production process [13]. The recovery of biomass includes high-energy demand processes like flocculation, filtration and sedimentation [11]. Furthermore, most microalgae are very small and have low cell densities, which makes the recovery process difficult [20].

The selection of a harvesting biomass method is very important to make commercial biofuels [26]. One of the main factors that influence the harvesting methods is the strain and species of microalgae. Algae with different characteristics require different harvesting methods. In general, harvesting is a two-step process: bulk harvesting and thickening. The first separates the biomass from the bulk suspension and the other one concentrates the slurry. The thickening process requires more energy than bulk harvesting because it involves techniques such as centrifugation and filtration [11].

Biomass conversion from microalgae

There are two technically viable conversion categories for algal biomass: thermochemical conversion and biochemical conversion. The choice of the conversion technique is based on factors such as the specie of algae, quantity of biomass and the desired final product [27]. Thermochemical conversion is based on the thermal decomposition of biomass to yield fuel products. Processes that can be used for this purpose include: combustion, gasification and pyrolysis [28]. Biochemical conversion techniques are: anaerobic digestion, alcoholic fermentation and photobiological hydrogen production [29]. Other methods for biomass recovery and conversion are actively being studied.

Membrane Technologies

Membrane technologies are being developed around the world for different applications. Some of these are municipal and industrial wastewater treatment, food processing wastewater, slaughterhouses wastewater and landfill leachates [30-33]. Nitrate removal from drinking water is another promising area for membrane bioreactor applications because membranes have several advantages compared to traditional denitrification methods [33, 34]. The membrane can reject microorganisms and some of the dissolved organic matter found in drinking water. Membranes can replace the post-treatment process that is currently being used in traditional drinking water treatment [35]. This emerging technology has several benefits such as: potential continuous separation and low energy consumption [36].

The developing applications and increase in new trends around the world regarding membrane technologies is an exciting and open-ended topic. A brief overview of some of the aspects regarding membranes is presented below. These include: membrane materials, membrane synthesis, membrane characterization and membrane fouling.

Membrane materials

Membranes are made out of different materials either biological or synthetic. Biological membranes are found in living organisms while synthetic ones can be made from organic or inorganic materials. The properties of the material should be taken into account when selecting a membrane material because these are directly related to the membrane separation capability.

Biological membranes serve different purposes to living organisms. The cell membrane is the most common biological membrane found and its functionality and structure is highly complex and differs from synthetic membranes [36]. Regarding synthetic membranes, some of the common organic membrane materials are polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polypropylene (PP), polyethylene (PE), polysulfone (PS), polyethersulfone (PES), polyacrylonitrile (PAN) and cellulose acetate (CA) [36]. On the other side, inorganic membrane materials frequently used are: ceramic, glass and metal.

Membrane synthesis

There are several ways to synthesize membranes. These include: phase inversion, (wet spinning and thermally induced phase separation) and stretching. Surface and subsurface characteristics are extremely important and must be controlled during membrane synthesis. Hollow fiber and multitubular membranes can be synthesized using either phase inversion or stretching. Ultrafiltration membranes are synthesized by phase inversion while either process can synthesize microfiltration membranes [37].

Membrane characterization

There are two types of membranes that are classified according to characteristics: porous and nonporous membranes.

Porous membranes contain pores, whose dimensions and distribution determine the separation capability of the membrane. Other factors that affect separation processes are concentration polarization, membrane fouling and pore geometry. Commonly found porous membranes are microfiltration and ultrafiltration membranes. Ionic membranes are porous membranes whose main characteristic is the presence of charged groups that determine the separation process, in addition to pore size and distribution. These membranes are commonly used in electric driven process but can also be used in nanofiltration, microfiltration and ultrafiltration processes. [36]

On the other side, nonporous membranes are capable of performing molecular level separations. The factor that affect the separation process are the chemical (mainly permeability) and physical properties of both the membrane and the permeate, and the interaction between these two [36].

Harvesting microalgal biomass using membrane technologies

Membrane technologies have been shown to be cheaper than centrifugation, or other harvesting methods for biomass recovery [38]. Other advantages of this emerging technology are the possibility to recycle CO₂ and nutrients, and the removal of protozoa and virus from the biomass [29]. Furthermore, no chemicals are required for the harvesting process, which prevents their accumulation in the biomass [39]. Several studies are being conducted around the world to provide an alternative for microalgae harvesting. Some have proven to be successful but the processes have not been scaled up for commercial production. Below is one example of a study conducted on microalgae using membrane technologies.

Submerged microfiltration membranes

A study to investigate the viability of harvesting 2 different species of microalgae using submerged microfiltration membranes was successfully conducted in Belgium.

Freshwater algae specie, *Chlorella vulgaris*, and a marine diatom, *Phaedactylum triconutum*, were used to identify the filtration performance of three membranes with a different porosity. Furthermore, the economic feasibility of the process was evaluated using data from a full-scale membrane bioreactor. The results showed a potential harvesting process with good filtration performance, low degree of membrane fouling and economic feasibility [40].

CHAPTER 3

MODEL

The purpose of this project was to identify the best combination of microalgae specie and membrane material to harvest algae using membrane technologies by modeling the total interaction energy of the microalgae and the membrane. The model was based on the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory in which the van der Waals (vdW) and electrostatic double-layer (EDL) interactions are combined to obtain the total interaction energy [41]. The mathematical expression used in this model for the total interaction energy was previously derived.

The EDL energy expression between a cylinder and a sphere was derived from the Poisson-Boltzmann equation [42, 43]. The Derjaguin approximation technique was used for the estimation of the energy between curved surfaces, because the original expression accounts for parallel flat plates equation plates [44] [45]. The surface element integration (SEI) technique was used to take into account the curvature effects of the surfaces because Derjaguin's technique only applies to large particles due to the assumption that the interaction energy is considerably shorter than the radii of curvature [41].

The vdW energy expression was also derived using the SEI technique [41]. Therefore in the model employed, the total interaction energy between a cylinder and a sphere was calculated using the SEI technique. The model was applied to 3 different species of microalgae and 5 hollow fiber membranes synthesized with different materials.

Theory

Surface Element Integration Technique

In the SEI technique the interaction energy (V) between two bodies with a separation distance D is calculated using a double integral over projected parallel planes from the surfaces of the bodies:

$$V(D) = \int_A \mathbf{n}_2 \cdot \mathbf{k}_2 \frac{\mathbf{n}_1 \cdot \mathbf{k}_1}{|\mathbf{n}_1 \cdot \mathbf{k}_1|} E(r) dA \quad (1)$$

where \mathbf{n}_1 and \mathbf{n}_2 are the outward unit vectors normal to the surfaces, \mathbf{k}_1 and \mathbf{k}_2 are the unit vectors directed toward the positive z axes of each body-fixed coordinate system. The coordinate system is selected in order for the xy planes to be parallel and the z axes facing each other. $E(r)$ is the interaction energy per unit area between two infinite flat plates, r is the separation distance between the infinite plates, and A is the projected area of the body on the xy plane [41].

Electrostatic Double Layer Energy

The EDL interaction energy (V_{EDL}) between a membrane and a microalgae with a separation distance D was calculated using the SEI technique. Since the radius of the cylinder (R_c) was greater than that of the sphere (R_s) for all the cases, the following expression was utilized:

$$\begin{aligned}
V_{EDL, sphere-cylinder}^{SEI}(D) = & 4\varepsilon_r \varepsilon_0 \kappa \psi_{o1} \psi_{o2} \int_0^{\frac{\pi}{2}} \int_0^{R_s} \frac{y \sqrt{R_c^2 - y^2 \sin^2 \theta}}{R_c} \times \\
& \left\{ \begin{aligned} & \csc h \left[\kappa \left(D + R_s - \sqrt{R_s^2 - y^2} + R_c - \sqrt{R_c^2 - y^2 \sin^2 \theta} \right) \right] \\ & - \csc h \left[\kappa \left(D + R_s + \sqrt{R_s^2 - y^2} + R_c - \sqrt{R_c^2 - y^2 \sin^2 \theta} \right) \right] \\ & - \csc h \left[\kappa \left(D + R_s - \sqrt{R_s^2 - y^2} + R_c + \sqrt{R_c^2 - y^2 \sin^2 \theta} \right) \right] \\ & + \csc h \left[\kappa \left(D + R_s + \sqrt{R_s^2 - y^2} + R_c + \sqrt{R_c^2 - y^2 \sin^2 \theta} \right) \right] \end{aligned} \right\} dy d\theta \\
& + \frac{\psi_{o1}^2 + \psi_{o2}^2}{2\psi_{o1}\psi_{o2}} \left[\begin{aligned} & -\coth \kappa \left(D + R_s - \sqrt{R_s^2 - y^2} + R_c - \sqrt{R_c^2 - y^2 \sin^2 \theta} \right) \\ & + \coth \kappa \left(D + R_s + \sqrt{R_s^2 - y^2} + R_c - \sqrt{R_c^2 - y^2 \sin^2 \theta} \right) \\ & + \coth \kappa \left(D + R_s - \sqrt{R_s^2 - y^2} + R_c + \sqrt{R_c^2 - y^2 \sin^2 \theta} \right) \\ & - \coth \kappa \left(D + R_s + \sqrt{R_s^2 - y^2} + R_c + \sqrt{R_c^2 - y^2 \sin^2 \theta} \right) \end{aligned} \right] \quad (2)
\end{aligned}$$

where ε_r and ε_0 are the relative permittivity of the solution and the permittivity of a vacuum, respectively; κ is the Debye-Hückel parameter of the electrolyte solution; ψ_{o1} and ψ_{o2} are the unperturbed surface potentials of the microalgae and the membrane, respectively; y is the radius of the circle, parallel to the xy plane, on the sphere and θ is the angle between the y axis and the line from the surface element to the center of the circle [41].

Van der Waals Energy

The vdW interaction energy (V_{vdW}) between a membrane and a microalgae with a separation distance D was calculated using the SEI technique. Since the radius of the cylinder was greater than the one of the sphere for all the cases, the following expression was utilized:

$$V_{vdW, sphere-cylinder}^{SEI}(D) = -\frac{A_H}{3\pi} \int_0^{\frac{\pi}{2}} \int_0^{R_s} \frac{y \sqrt{R_c^2 - y^2 \sin^2 \theta}}{R_c} \times$$

$$\left\{ \begin{array}{l} 1 / \left(D + R_s - \sqrt{R_s^2 - y^2} + R_c - \sqrt{R_c^2 - y^2 \sin^2 \theta} \right)^2 \\ -1 / \left(D + R_s + \sqrt{R_s^2 - y^2} + R_c - \sqrt{R_c^2 - y^2 \sin^2 \theta} \right)^2 \\ -1 / \left(D + R_s - \sqrt{R_s^2 - y^2} + R_c + \sqrt{R_c^2 - y^2 \sin^2 \theta} \right)^2 \\ +1 / \left(D + R_s + \sqrt{R_s^2 - y^2} + R_c + \sqrt{R_c^2 - y^2 \sin^2 \theta} \right)^2 \end{array} \right\} dy d\theta \quad (3)$$

where A_H is the Hamaker constant for the integrated media [41].

Methodology

Microalgae

Three different species of microalgae were used in the model: *Chlorella* sp., *Nannochloris Oculata* and *Scenedesmus Obliquous*. The zeta potential of each specie is - 23.73 mV, -27 mV and -7 mV respectively, according to the literature [46-48]. The shape of the algae species varies but it was assumed that all of them were perfect spheres. The average cell diameter for *Chlorella* was found to be $3.13 \pm 0.80 \mu\text{m}$: thus, a radius of $1.565 \mu\text{m}$ was used in the model [48]. The average size diameter for *Nannochloris* was found to be between 3 and $4 \mu\text{m}$. Consequently, a radius of $1.75 \mu\text{m}$ was used in the model [49]. The average diameter for *Scenedesmus* was found to be $3 \mu\text{m}$. Therefore, a radius of $1.5 \mu\text{m}$ was utilized in the model [50].

Hollow Fiber Membrane

Hollow fiber membranes were selected due to their cylindrical shape. Five different materials were chosen to be modeled: cellulose acetate (CA), cellulose acetate butyrate (CAB), cellulose acetate propionate (CAP), poly(vinylbutyral) (PVB) and Polyamide type 84 (P84). These particular materials were selected because their zeta

potential was found in the literature. The zeta potential of the membranes used is -18, -15, -10, -8 and -21.5 mV respectively, according to the literature [51-53]. The outer radius of the hollow fiber membrane was kept constant at 790 μm [53].

CHAPTER 4

RESULTS AND DISCUSSION

Matlab was used in order to model the energy interactions between microalgae and hollow fiber membranes. The Hamaker constant was assumed to be 5 kT taking into account that most reported Hamaker constants are between 1 and 10 kT between a particle and a filter across water [41]. The 5 different membrane materials were analyzed for each microalgae in order to identify the best possible harvesting combination (lowest energy barrier). For each microalgae, the zeta potential of each membrane material was the only variable in the model, as the radii of all membranes were kept constant.

Low barrier energy means attachment of particles to the membrane surface. Particles on the membrane surface is one of the most common membrane fouling mechanism, therefore, in most membrane technology applications, such as wastewater treatment, a higher energy barrier between particles and membrane surfaces is wanted [41]. The objective of this project was to find the algae that would best attach to a certain membrane material thus low barrier energy was desired.

The energy barrier was calculated in kT units where k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ m}^2 \text{ kg} / \text{s}^2 \text{ K}$) and T is the absolute temperature (298 K), thus 1 kT is equivalent to $4.1143 \times 10^{-21} \text{ Joules}$.

Membrane Material Selection

The total DLVO interaction energy between microalgae and hollow fiber membranes of different materials was calculated using the model previously mentioned. Figures 1, 2 and 3 show the effect of the zeta potential of the hollow fiber membrane material on the total DLVO interaction between the *Chlorella*, *Nannochloris* and *Scenedesmus*, and the membrane, respectively.

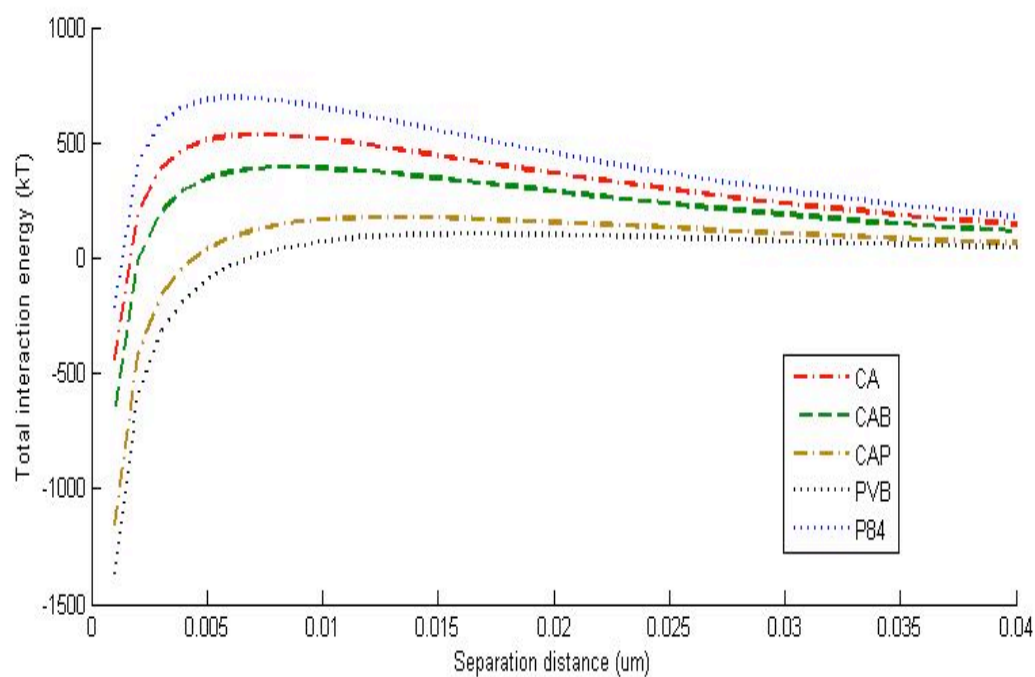


Figure 1: Effect of zeta potential of membrane materials on the total interaction energy between Chlorella and a hollow fiber membrane.

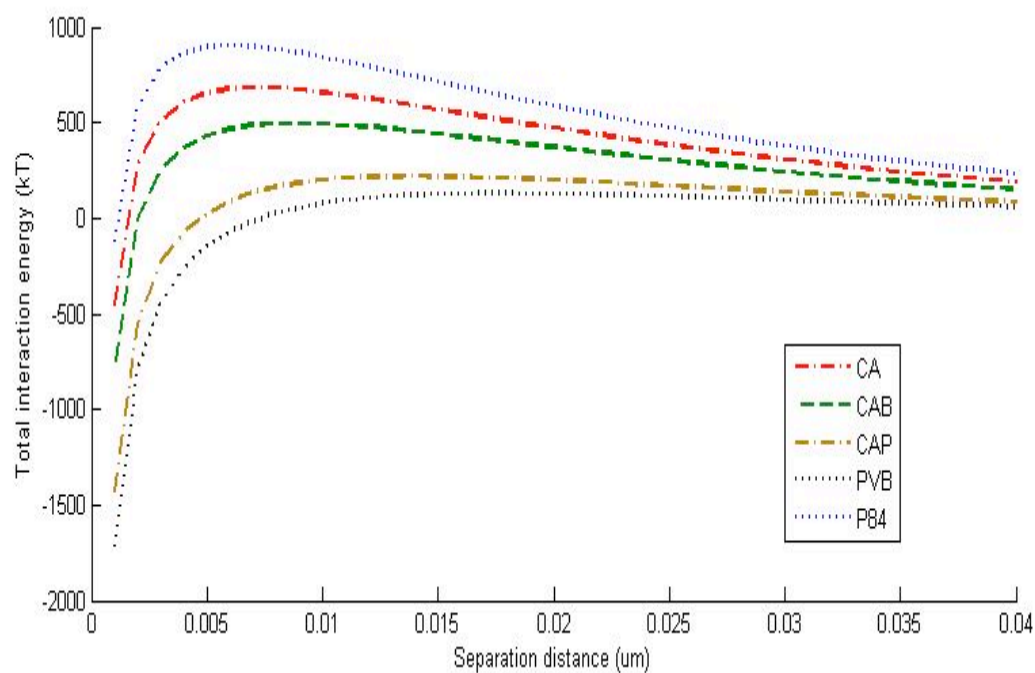


Figure 2: Effect of zeta potential of membrane materials on the total interaction energy between Nannochloris and a hollow fiber membrane.

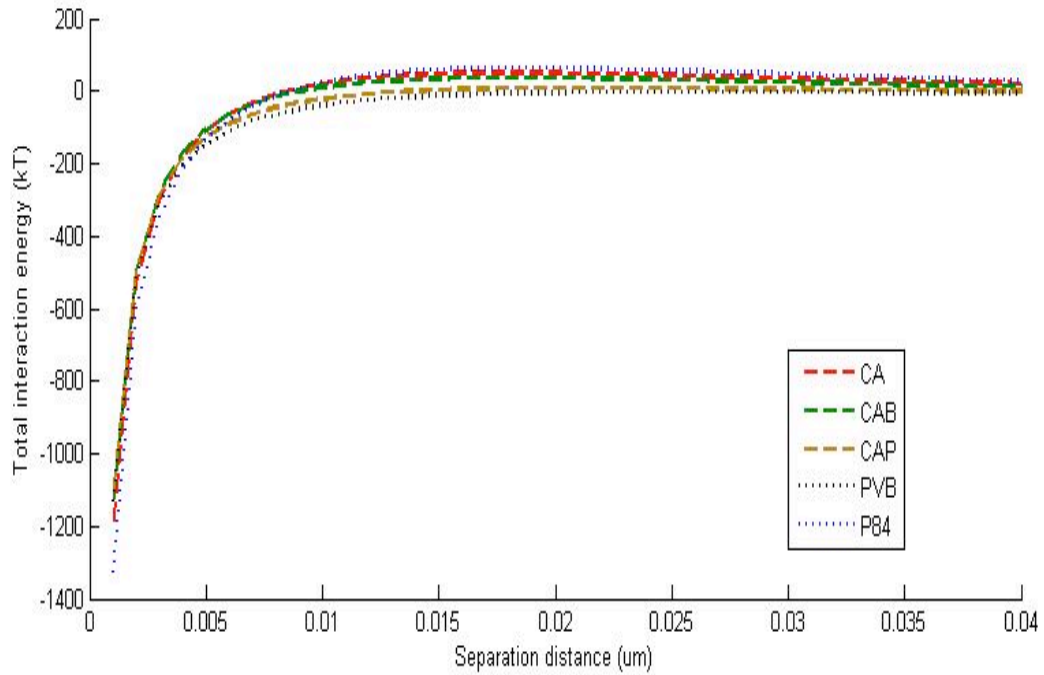


Figure 3: Effect of zeta potential of membrane materials on the total interaction energy between *Scenedesmus* and a hollow fiber membrane.

As observed in Figures 1, 2 and 3, the energy barrier between the microalgae and the hollow fiber membrane increases as the zeta potential of the membrane material decreases. This means that the microalgae attaches better to a membrane material with a higher zeta potential. In the case of the modeled membrane materials, all the microalgae had lower total interaction energy with the PVB membrane compared to the rest.

Microalgae Selection

The total DLVO interaction energy between the PVB hollow fiber membrane and the 3 species of microalgae modeled was compared to one another in order to obtain the best combination for algae harvesting on the modeled membrane materials. Table 1 summarizes the total DLVO energy barrier between the 3 microalgae and 5 hollow fiber membrane materials studied.

Table 1: Total DLVO interaction energy in kT between different microalgae and membrane materials

Membrane Material	Algae: Chlorella	Nannochloris	Scendesmus
CA	534.8203	683.1977	50.2007
CAB	393.4589	496.4092	36.1415
CAP	176.4653	219.0700	8.3041
PVB	104.5159	130.0346	-2.7834
P84	696.4297	903.8113	63.4754

The anti barrier energy was found to be lower for the Scendesmus compared to the other 2 species. Smaller particles are more likely to attach to the membrane because the energy barrier decreases as the particle size decreases [41]. Therefore the modeling results agree with previous studies of energy interaction between particles and membranes. Another factor influencing the total energy barrier is the zeta potential of the microalgae, which was lower for Scendesmus than the other 2 species. The radius of the algae does not change much between species. Thus, the zeta potential is a more important factor than particle size when determining the total DLVO interaction energy.

CHAPTER 5

CONCLUSION

An alternative and more sustainable method to supply the immense energy demand is necessary in order to reduce or eliminate the negative impact on the environment and the depletion of natural resources. Biofuel production from microalgae is one of the most promising alternatives but a commercially feasible cultivation method is not available yet. This study aimed to introduce a method to recover algal biomass using membrane technologies.

In this study, the DLVO model derived using the SEI technique was used to identify the interaction energy in kT between microalgae and hollow fiber membranes. Three different microalgae species and 5 membrane materials were modeled in order to identify the best combination of microalgae and membrane material to harvest microalgae for biomass extraction. Based on the model, it was predicted that *Scenedesmus Obliquus* would have the lowest interaction energy barrier (-2.7834 kT) with a PVB hollow fiber membrane. Thus this specie would have the greatest initial number of cells attaching to the mentioned membrane compared to other species and membrane materials. Further work should be done in order to integrate algae growth and biomass harvesting to the existing model.

CHAPTER 6

FUTURE WORK

The modeling portion of this method to recover algal biomass using membrane technologies is comprised of three main steps. This study presented only the first step where the microalgae specie and hallow fiber membrane material were selected based on the modeling results. In further studies other parameters can be taken into account such as the membrane diameter. The next step in the process would be to identify how much can algae grow attached to the membrane based on water and nutrient supply. In order to obtain this information it would be important to calculate the membrane flux. The last step of the modeling process would be to identify how much biomass can be extracted from the harvested microalgae.

After the method has been modeled, the predictions should be validated with experimental work in order to determine if this method is feasible. If that were the case, the method of growing microalgae using membrane technologies to recycle water, nutrients and CO₂ could be scaled up for the production of biofuels.

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